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ORGANOMETALLIC CARBOSILANE POLYMERS CONTAINING VANADIUM  
AND THEIR PREPARATION

S. Yajima, K. Okamura, T. Shishido and K. Fukuda

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16. Abstract  The present invention concerns a new aorganometallic polymer material containing in part a vanadium-siloxane linkage (V-O-Si), which has excellent resistance to heat and oxidation and a high "reside ratio" after high temperature treatment in a non-oxidizing atmosphere, for example, nitrogen, argon, helium, ammonia, or hydrogen.  ORIGINAL PAGE IS OF POOR QUALITY			
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Organometallic carbosilane polymers containing vanadium  
and their manufacture.

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Invention of: Seishi Yajima, Kiyohito Okamura, Toetsu Shishido,  
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The present invention concerns a new aorganometallic polymer \*/1 material containing in part a vanadium-siloxane linkage (V-O-Si), which has excellent resistance to heat and oxidation and a high "reside ratio" after high temperature treatment in a non-oxidizing atmosphere, for example, nitrogen, argon, helium, ammonia, or hydrogen.

Various processes have been proposed before now for the production of polycarbosilanes with a Si-CH<sub>2</sub> backbone in the main structural chain and with an organic side chain attached to the silicon atom. For example, Fritz described a method for manufacturing a polycarbosilane from a monosilane on page 657 of the paper in Angew. Chem. 79 (1967); U. S. patent 4,052,430 describes a process for manufacturing a polycarbosilane from a polysilane, the operation taking place in an autoclave; and U. S. patent 4,220,600 describes a polycarbosilane containing in part a siloxane bond which can be obtained by a process which does not require use of an autoclave.

The present applicant has now found that one can obtain new organometallic polymer materials formed principally of carbosilane and containing in part a vanadium-siloxane bond which have better resistance to heat and oxidation and higher reside ratio after treatment at high temperature than do present polycarbosilanes, by causing the reaction of a polysilane with a polyvanadosiloxane or a vanadium complex in which a coordination atom next to the vanadium atom is oxygen.

The present invention thus brings forth a new organometallic polymer material in which the framework of the main chain consists of Si-CH<sub>2</sub> and V-O bonds with, in part, a vanadium-siloxane linkage, the ratio of silicon to vanadium atoms being between 3 and 1000, the side chain directly attached to the silicon atom being selected from hydrogen or methyl, ethyl, or phenyl groups and the vanadium /2

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atom being attached to the silicon through an oxygen atom with practically no organic side chain attached directly to the vanadium.

The invention also contains a process for producing these new organometallic polymers, according to which a polyvanadidosiloxane or a vanadium complex in which oxygen is one coordination atom adjoining the vanadium atom is mixed with a polysilane of formula



in which  $R_1$  and  $R_2$ , which can be identical or different from each other, represent hydrogen or a methyl, ethyl or phenyl group--provided  $R_1$  and  $R_2$  are not both hydrogen--and  $n$  is a number not greater than 500; this mixture is caused to react at 250 to 500°C in a non-oxidizing atmosphere.

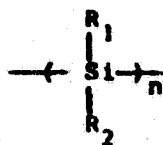
Figure 1 of the attached drawings is an infrared absorption spectrum of the organometallic polymer of this invention.

Figures 2 and 3 are infrared absorption spectra of previously known polycarbosilanes, presented for comparison, and

Figure 4 compares results of thermogravimetric analysis of the organometallic polymer of this invention and of the previously known polycarbosilane.

We begin by describing the present process.

In this process one starts with a polysilane of the following formula:

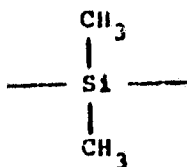


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This polysilane can have a structure which is linear or cyclic or mixed--that is, both linear and cyclic--and in the formula shown the number  $n$  is ordinarily equal to at least three ( $n \geq 3$ ), and preferably  $5 \leq n \leq 100$ . The sequence of the lateral chains  $R_1$  and  $R_2$ --that is, hydrogen and methyl, ethyl and phenyl groups--is optional.

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A particularly appropriate polysilane is the one formed only from

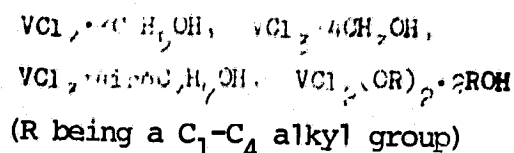


units or even from a polysilane in which at least 50% of the side chains are methyl groups, with the others phenyl groups and/or hydrogen. For linear polysilanes the terminal groups will preferably be OH or  $\text{CH}_3$ .

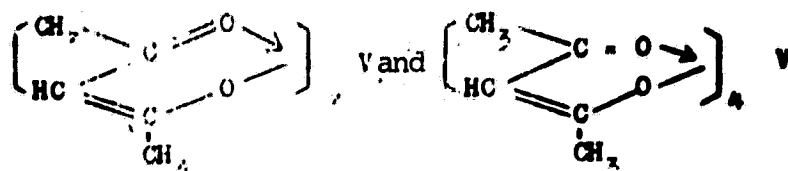
The other starting material in the present process which is reacted with the polysilane is a polyvanadidosiloxane or a vanadium complex.

Polyvanadidosiloxane is a polymeric material which can be obtained by the process described in U. S. patent application 210,639 of November 26, 1980 in the name of Yajima et al, and in which the skeleton of the main chain consists of Si-O and V-O bonds.

The vanadium complex is a compound in which one coordination atom next to the vanadium is oxygen; some examples of such a complex are the following:



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This vanadium complex with a coordination atom next to the vanadium being oxygen can be obtained by one of the following methods, for example:

(1) an inorganic vanadium compound is reacted with a complexing agent which can easily complex with this vanadium compound; examples of the latter include vanadium halides such as  $\text{VCl}_4$ ,  $\text{VCl}_3$ , and  $\text{VCl}_2$ , oxysulfates such as  $\text{VOSO}_4$ , oxyoxylates such as  $\text{VOCl}_2\text{O}_4$ , sulfates such as  $\text{V}_2(\text{SO}_4)_3$ , oxyhalides such as  $\text{VOBr}_2$ , as well as the ammonium or alkali-metal salts of these compounds, such as  $\text{NaVOCl}_4$ ,  $\text{NH}_4\text{V}(\text{SO}_4)_2$  and  $\text{KVO}(\text{C}_2\text{O}_4)_2$ . Examples of complexing agents include the following:

$\text{C}_4\text{H}_8\text{O}$  (tetrahydrofuran),  $\text{CH}_3\text{OH}$ ,  
 $\text{C}_5\text{H}_8\text{O}_2$  (acetylacetone)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ ,  $n\text{-C}_4\text{H}_9\text{OC}_4\text{H}_9$ ,  
 $(\text{CH}_2\text{OH})_2$ ,  $\text{CH}_3\text{COCH}_3$ ,  $\text{C}_5\text{H}_5\text{OH}$ ,  $\text{C}_5\text{H}_4\text{O}_2$  (pyrone),  
 $\text{C}_7\text{H}_6\text{O}$  (benzaldehyde),  $\text{C}_7\text{H}_6\text{O}_2$  (benzoic acid) and  
 $\text{C}_7\text{H}_8\text{O}$  (benzyl alcohol).

In general, to react the vanadium compound with the complexing agent, it is sufficient to dissolve the former in the latter, with or without heating. In the complex used in this invention the valence of the vanadium can be 2, 3, 4 or 5.

Because of its greater reactivity with the polysilane, it is preferable to take a product resulting from dissolution of a complex vanadium salt, such as vanadium acetylacetonate, in a complexing agent such as those listed above, so that it will react again.

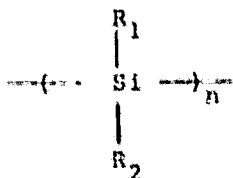
(2) an organic compound of vanadium such as  $\text{V}_2\text{OCl}_4(\text{OR})_2$ ,  $\text{V}(\text{OR})_n$ ,  $\text{VO}_x(\text{OR})_{4-x}$  (R is a  $\text{C}_1\text{-C}_4$  alkyl group; n is 3, 4 or 5; and x is 1 or 2),  $\text{VCl}(\text{OCH}_3)_2$ , or  $\text{VOCl}_2(\text{OC}_2\text{H}_5)$  is dissolved in a lower alcohol such as methanol, ethanol, n-propanol, i-propanol,



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n-butanol, sec-butanol, or t-butanol, and in this way one can also obtain the vanadium complex used in accordance with this invention.

In the present process the organometallic polymer is obtained by mixing the polyvanadosiloxane, or the vanadium complex in which one coordination atom next to the vanadium is oxygen, with one or more polysilanes of the formula



and heating the mixture between 250-500°C in a non-oxidizing atmosphere to accomplish polymerization.

It is necessary that the elevated temperature polymerization take place in a non-oxidizing atmosphere; otherwise--for instance, if it is carried out in air--the polysilane undergoes oxidization and the reaction does not proceed adequately. The inert, for example, nitrogen, argon and helium, which are easy to use, are especially preferable.

Ordinarily, it is preferable that the reaction take place at or near atmospheric pressure because if it is carried out in vacuo or at a very reduced pressure, the low molecular-weight components are eliminated from the reaction system by distillation which leads to a considerable reduction in the yield of the product sought. It is also preferable to carry out the polymerization by introducing the non-oxidizing gas into the reactor at a fixed flow which allows the pressure inside the apparatus to be held close to atmospheric and avoids a temperature rise or a pressure increase due to evolution of a gas such as methane during the course of the reaction.

The polymerization temperature is generally 250-500°C because the reaction does not go easily below 250°C and above 500°C, the organometallic polymer formed begins to take on an inorganic character because of progressive elimination of side chains.

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The ratio of polysiloxane and vanadium compound (polyvanadio-siloxane or vanadium complex) is chosen so that the ratio of silicon atoms to vanadium atoms in the final organometallic polymer will lie between 3 and 1000.

The time to accomplish thermopolymerization in the present process is generally 1 to 10 hours, the reaction coming to an end in 10 hours.

Carrying out the process requires only a simple reactor with reflux system, etc., but needs no special attachments such as pressure-tight receivers or a recirculation system.

The organometallic polymer so obtained can be purified by dissolving it in a solvent such as n-hexane, benzene, xylene or tetrahydrofuran, then filtering the solution and evaporating the solvent. If necessary, the purified product can even be distilled and concentrated at atmospheric pressure or under reduced pressure at a temperature of 50-450°C.

We now describe the organometallic polymer obtained which contains in part a vanadium-siloxane linkage.

The organometallic polymer obtained according to Example 1 below, starting with polydimethylsilane, gives the infrared absorption spectrum shown in Figure 1 of the attached drawings; for comparison, Figure 2 gives the infrared absorption spectrum of a polycarbosilane formed by treatment of polydimethylsilane in an autoclave for 36 hours at 470°C under a pressure of 36 atm of argon, following the method described in U. S. patent 4,052,430, cited above. Figure 3 shows the infrared absorption spectrum of a polycarbosilane with part siloxane linkage, obtained by mixing 250 g polydimethylsilane with 10 g of a polyborodiphenylsiloxane, heating the mixture to 370°C in a stream of nitrogen and polymerizing for five hours, in accordance with the method described in U. S. patent 4,220,600 cited above.

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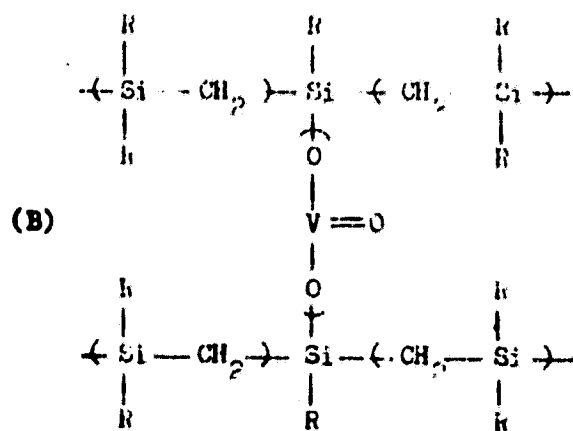
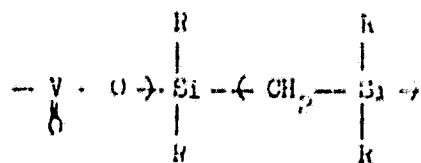
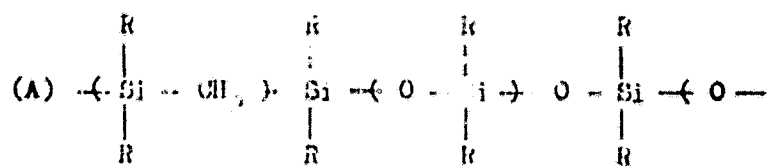
The infrared absorption spectrum of Figure 1 has C-H absorption at 2950 and 2900  $\text{cm}^{-1}$ , Si-H at 2100  $\text{cm}^{-1}$ , Si-CH<sub>3</sub> at 1260 and 800  $\text{cm}^{-1}$ , and Si-CH<sub>2</sub>-Si at 1040  $\text{cm}^{-1}$ , as well as new absorption peaks at 3400, 1600, 1180, 960, 880, 740 and 490  $\text{cm}^{-1}$ , attributable to the Si-O-V linkage--new peaks which do not appear in the spectra of the polycarbosilane (Figure 2) or the polycarbosilane with part siloxane linkage (Figure 3).

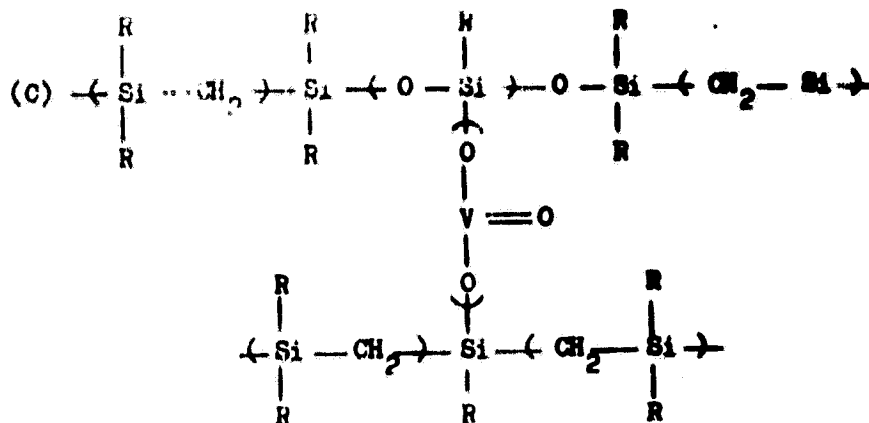
Electron microscopic observations of the organometallic polymer obtained in Example 1 show the absence of crystallinity in the bright field image and the results of X-ray powder diffraction and of electron diffraction show absence of formation of solid vanadium oxide. These experimental results allow us to conclude that almost all of the vanadium atoms are in the form Si-O-V.

A very special difference between the organometallic polymers of this invention and the previously known polycarbosilanes is that the backbones of the former consist of Si-CH<sub>2</sub> and V-O bonds, and when they are strongly heated in a non-oxidizing atmosphere, cross-linking occurs between 300-350°C through the vanadiosiloxane portion of the molecule, which increases their cross-link density and hinders their decomposition by heat. Thus, after strong heating, their "residue ratio" remains high--that is, the weight loss is low. This appears clearly in the results of thermogravimetric analyses shown in Figure 4, in which Curve A is for the organometallic polymer of Example 1, and Curve B is for the polycarbosilane with partial siloxane linkage, obtained by the method described in U.S. Patent 4,220,600 cited above. /8

The structure of the organometallic polymers of this invention is complex and it cannot be entirely established exactly at the present technological state of chemical investigations. Nevertheless, the present applicant assumes that they have partial structures of which the following are examples:

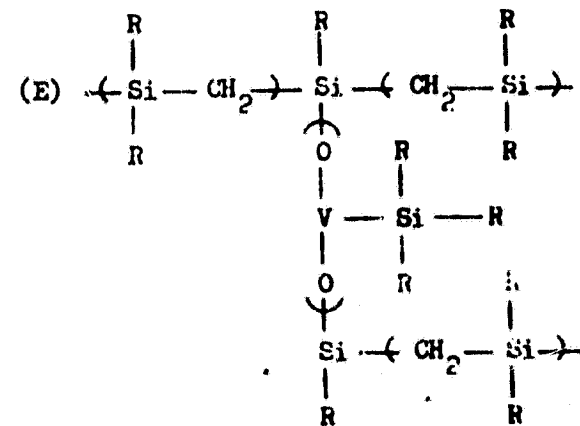
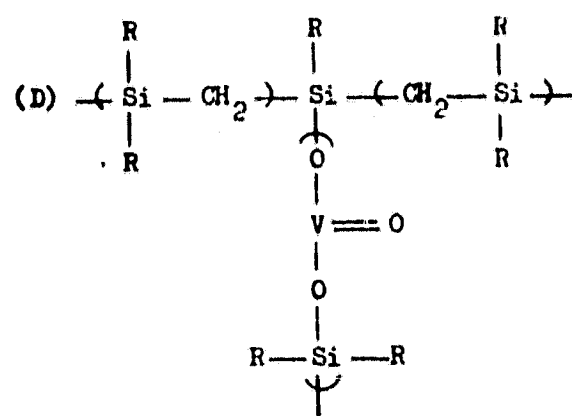
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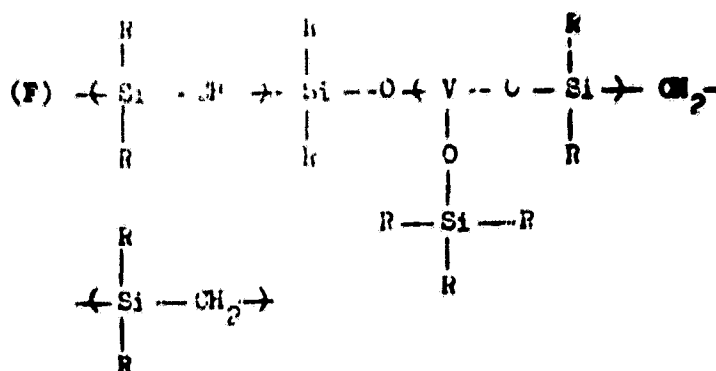




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In these formulas the symbol R represents a methyl, ethyl or phenyl group, or hydrogen; the various R groups can be identical or different from each other.

In these examples of partial structures of the present organometallic polymers with the backbone of the main chain composed of Si-CH<sub>2</sub> and V-O bonds, an atom of tri- or tetravalent vanadium is bound to the silicon atom through an oxygen atom. In general, the stable valence of the vanadium in these polymers is the trivalent or tetravalent state, but there can also be an atom of divalent vanadium.

The X-ray powder diffraction patterns of the organometallic polymers of this invention show that they are amorphous, as are the previously known polycarbosilanes. When such a polymer is strongly heated in a non-oxidizing atmosphere, for example, gaseous argon, helium, hydrogen, ammonia or nitrogen, it is converted mainly into β-SiC containing vanadium, and X-ray powder diffraction analysis of the product resulting from this heating (of the organometallic polymer of Example 1) to 1400°C for one hour in a stream of argon, using a nickel filter and a copper anode as the X-ray source, shows mainly β-SiC and some graphite. The presence of vanadium was found in this product by a wet colorimetric method.

Elemental analysis of the present polymers gives the following general contents of the various elements by weight: /11

Si : 16 - 60, C : 20 - 60, O : 0,5 - 3, H : 5 - 10,  
V : 0,01 - 15 %.

Study of the molecular-weight distribution by gas chromatography shows a range from 500 to 100,000 and the number-average molecular weight determined by vapor pressure is from 1400 to 2200.

Organometallic polymers in which the backbone of the main chain consists of Si-CH<sub>2</sub> and V-O bonds are thermoplastic materials soluble in such organic solvents as n-hexane, xylene, tetrahydrofuran and benzene; they melt between 60-300°C. They can thus be formed in an ordinary single-axis press, an isostatic press, an injection mold, etc., or even by extrusion. The formed articles are heated in a non-oxidizing atmosphere at not less than 800°C to be partially transformed into silicon carbide, SiC. Sintered cast articles can also be obtained by impregnating an inorganic article which has been strongly heated, or prepared separately, with a melt of the present organometallic polymer resulting from heating in a non-oxidizing atmosphere, or even with a solution of this polymer in an organic solvent, then heating the impregnated article to between 1300-1800°C in a non-oxidizing atmosphere, which fills the pores of the inorganic article with silicon carbide, SiC.

The new organometallic polymers of this invention, in which the backbone of the main chain is formed of Si-CH<sub>2</sub> and V-O bonds, in part with a vanadium-siloxane linkage and which have excellent resistance to heat and oxidation, are very valuable for forming continuous filaments, films, coatings and powders composed principally of silicon carbide, due to the fact that following very strong heating in a non-oxidizing atmosphere their residue ratio remains high--that is, weight loss is low.

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In Table I are the properties and characteristics of the organometallic polymer of Example 1 which are compared with those of the

TABLE 1

Properties	polycarbosi- silane (U.S. patent 4,052,430)	polycarbosi- silane with partial silo- xane linkages (U.S. Patent 4,220,600)	new organomet- allic polymer of this invention, from Example 1
number average molecular wt.	1800	1720	1900
decomposition temperature, °C	310	350	370
weight gain by oxidation after holding at 200°C for 1 hr in air	9.0	6.5	6.0
residue ratio of material after holding 1 hr. at 1500°C in argon	49.8	73.8	75.0

polycarbosilane formed from polydimethylsilane in an autoclave at 470°C for 14 hours with the final pressure in the apparatus 110 atmospheres, following the method described in U.S. Patent 4,052, 430 cited above; also included are data for polycarbosilane containing in part siloxane linkages formed from polydimethylsilane and 3.85 weight percent polyborodiphenylsiloxane at 400°C for five hours in a nitrogen atmosphere, by the method described in U.S. Patent 4,220,600 cited above.

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The results in Table 1 show that the properties of the organometallic polymer of this invention are superior to those of the polycarbosilanes of the prior technique.

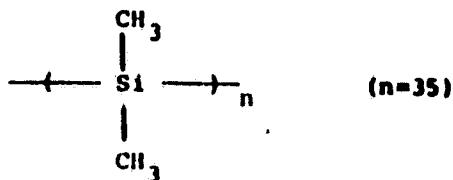
The following examples are given to illustrate the present invention.

#### Example 1



In a beaker, 40 ml of a solution of 25 g  $\text{VCl}_4$  in 500 ml tetrahydrofuran is added to 20 g of an  $\alpha$ ,  $\omega$ -dihydroxy-polydimethylsiloxane with an average degree of polymerization of 500. The mixture is heated to  $190^\circ\text{C}$  on a hot plate and the heating is stopped when the mixture has become very viscous. The hot mixture is then filtered and tetrahydrofuran is added to the filtrate to make a total volume of 100 ml.

20 grams of polydimethylsilane of the formula



is weighed out into a 200 ml round-bottom flask, the 100 ml of the tetrahydrofuran solution prepared above is added and the mixture is stirred under nitrogen and heated to 200°C to evaporate the tetrahydrofuran.

Next a 100 ml round-bottom flask is fitted with a reflux condenser. The bottom of the flask is held at 400°C, with a nitrogen atmosphere; the reaction is carried out in an electric oven by holding the mixture at 400°C for five hours.

After the reaction, xylene is added, the solution is filtered at atmospheric pressure and the product is transferred to a round-bottom separable 200 ml flask fitted with a Liebig condensor for distillation. With constant stirring, a current of nitrogen is passed through the flask while the product is being heated with a heating mantle.

The xylene is distilled off (boiling point 140°C), then the temperature is slowly raised to 320°C at 10°C per 10 minutes to eliminate low molecular-weight organometallic polymer and to concentrate the product.

These operations produce 12 g of concentrated product, whose infrared absorption spectrum is shown in Figure 1 of the attached drawings.

Elemental analysis of this organometallic polymer has given the following results:

Si : 50 weight percent  
C : 38 weight percent  
H : 6 weight percent  
O : 4.8 weight percent  
V : 1.0 weight percent

After heating (calcination) this polymer in an argon atmosphere from room temperature to 1500°C, the residue amounts of 75% of the starting weight, and X-ray powder diffraction (nickel-filtered Cu K $\alpha$ ) of the calcined product shows that this material is composed chiefly of  $\beta$ -SiC, with some  $\alpha$ -SiC and graphite. Vanadium was found by wet colorimetry.

Gas chromatography shows a molecular-weight distribution of 500 to 100,000 for this organometallic polymer and a vapor-pressure measurement gave a number average molecular weight of 1900.

#### Example 2

40 grams of the same polydimethylsilane as in Example 1 is mixed in a 100 ml round-bottom flask with 15 ml of a VCl<sub>4</sub>/tetrahydrofuran complex formed by dissolving 25 ml of VCl<sub>4</sub> in 500 ml tetrahydrofuran.

A rotary evaporator is then attached to the flask and the tetrahydrofuran is evaporated at 60°C over a water bath and at a reduced 15 pressure of 50 mm Hg (66.5 hPa) obtained with a water aspirator. Then, returning to Example 1, one obtains an organometallic polymer which is filtered and concentrated, giving 26 g of final product.

After this product has been heated from room temperature to 1400°C at 5°C/min, thermogravimetric analysis of the heated product shows that 65% of the original weight remains.

#### Example 3

A solution of 6.5 g vanadyl sulfate ( $\text{VOSO}_4$ ) in 100 ml acetylacetone is carefully mixed with 50 g of a polysilane in which the ratio of methyl to phenyl groups in the side chains is 70/30. The acetylacetone is evaporated by distillation and the dry powder so obtained is placed in a three-neck flask fitted with a stirrer. While a stream of argon is flowing through the flask, it is heated to  $500^\circ\text{C}$  to melt the powder, which then polymerizes over 10-1/2 hours.

The polymer so formed is dissolved in tetrahydrofuran and the resulting solution is filtered. The tetrahydrofuran is then evaporated in a stream of nitrogen and the remaining material is concentrated at  $350^\circ\text{C}$  for one hour.

The organometallic polymer obtained in this way have a number average molecular weight of 2013 and after it has undergone heating to  $1700^\circ\text{C}$  for one hour under argon, 70% of the original weight remains.

#### Example 4

100 grams of polydimethylsilane with a degree of polymerization of 50 and 3 g vanadyl oxalate ( $\text{VO}_2\text{C}_2\text{O}_4$ ) are carefully ground, then mixed under a stream of argon. The mixture is placed in a reaction vessel fitted with a reflux condenser, nitrogen is passed through the mixture and the polymerization reaction is run at  $370^\circ\text{C}$  for six hours.

After the polymer so obtained had been heated from room temperature to  $1400^\circ\text{C}$  in a stream of argon, the change in weight was determined: 72% of the original weight was found to remain. X-ray powder diffraction of the product identified it as formed of  $\beta$  silicon carbide ( $\text{SiC}$ ) and graphite. /16

CLAIMS

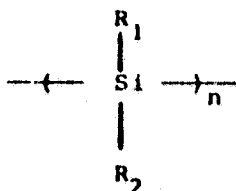
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1. Organometallic polymeric material in which the backbone of the main chain consists of Si-CH<sub>2</sub> and V-O bonds, in part with a vanadium-siloxane linkage, the ratio of number of silicon to vanadium atoms lying between 3 and 1000, the side chain directly attached to the silicon atom being chosen from hydrogen and methyl, ethyl and phenyl groups, and the vanadium atom linked to the silicon through an oxygen atom, with practically no organic side chain attached directly to the vanadium.

2. Polymer of Claim 1, melting between 60 and 300°C.

3. Polymer of Claims 1 or 2, soluble in organic solvents.

4. Process for production of organometallic polymers of Claim 1, characterized by the fact that a polyvanadiosiloxane, or a vanadium complex in which one coordination atom next to vanadium is oxygen, is mixed with a polysilane of formula



in which R<sub>1</sub> and R<sub>2</sub> are identical or different from each other, and represent hydrogen or a methyl, ethyl or phenyl group, with the condition that R<sub>1</sub> and R<sub>2</sub> are not both hydrogen, and n is a number not greater than 500, and the mixture is reacted at a temperature of 250 to 500°C in a non-oxidizing atmosphere.

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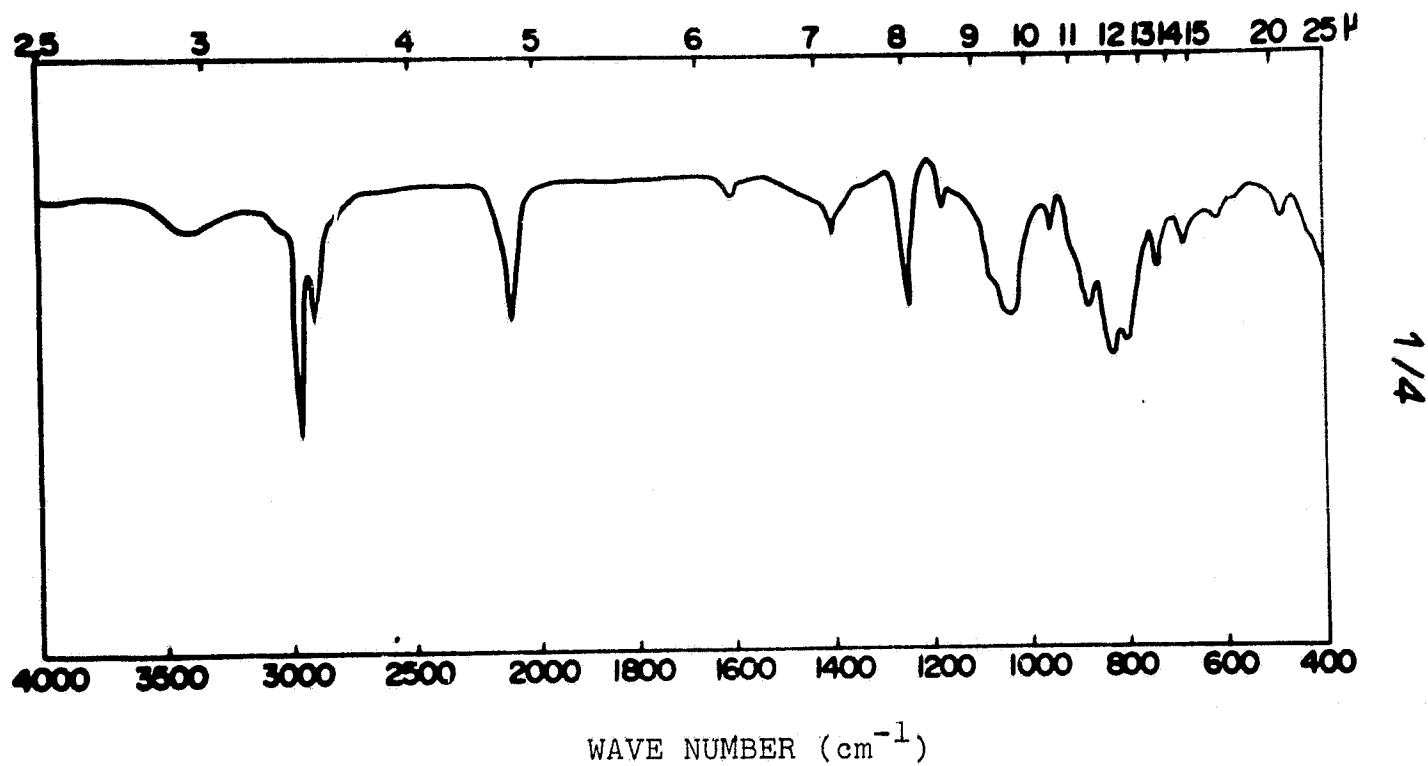


FIG. 1

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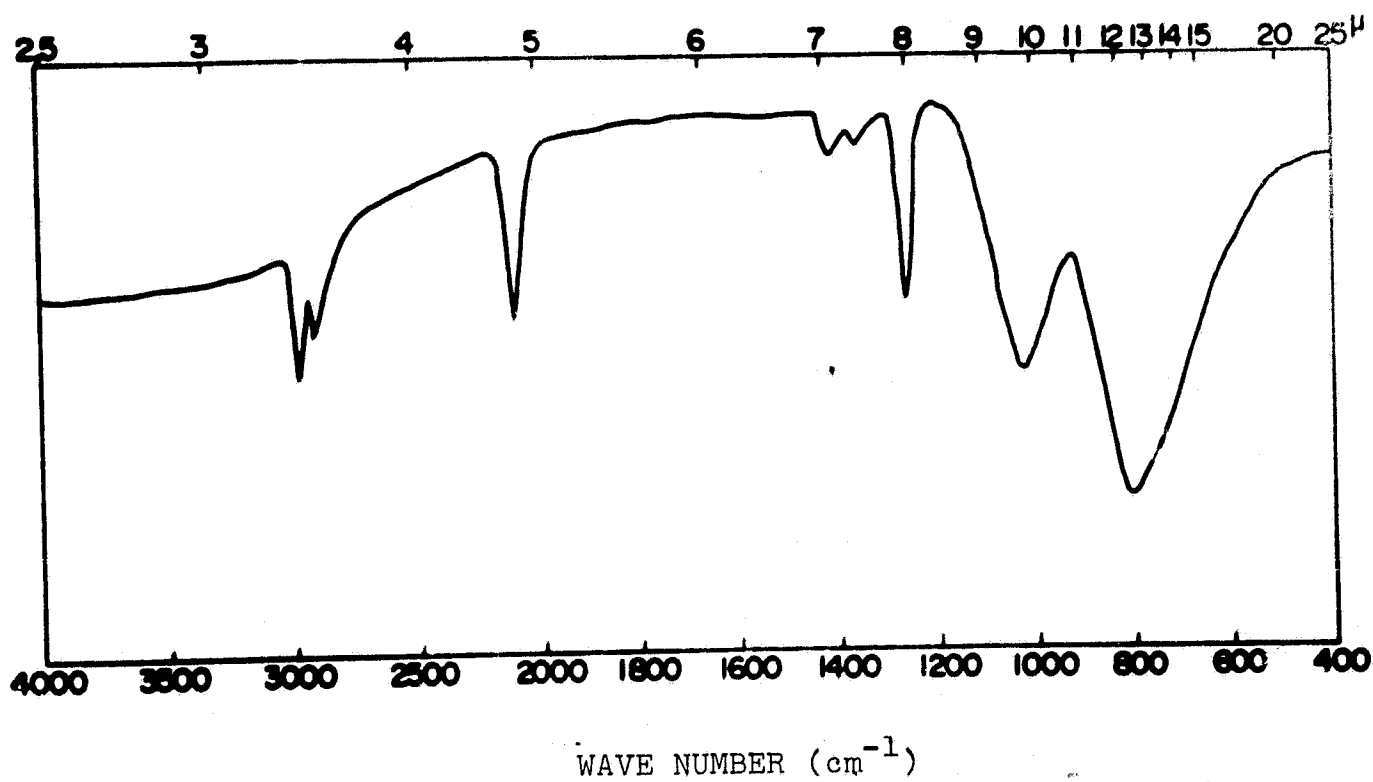


FIG. 2

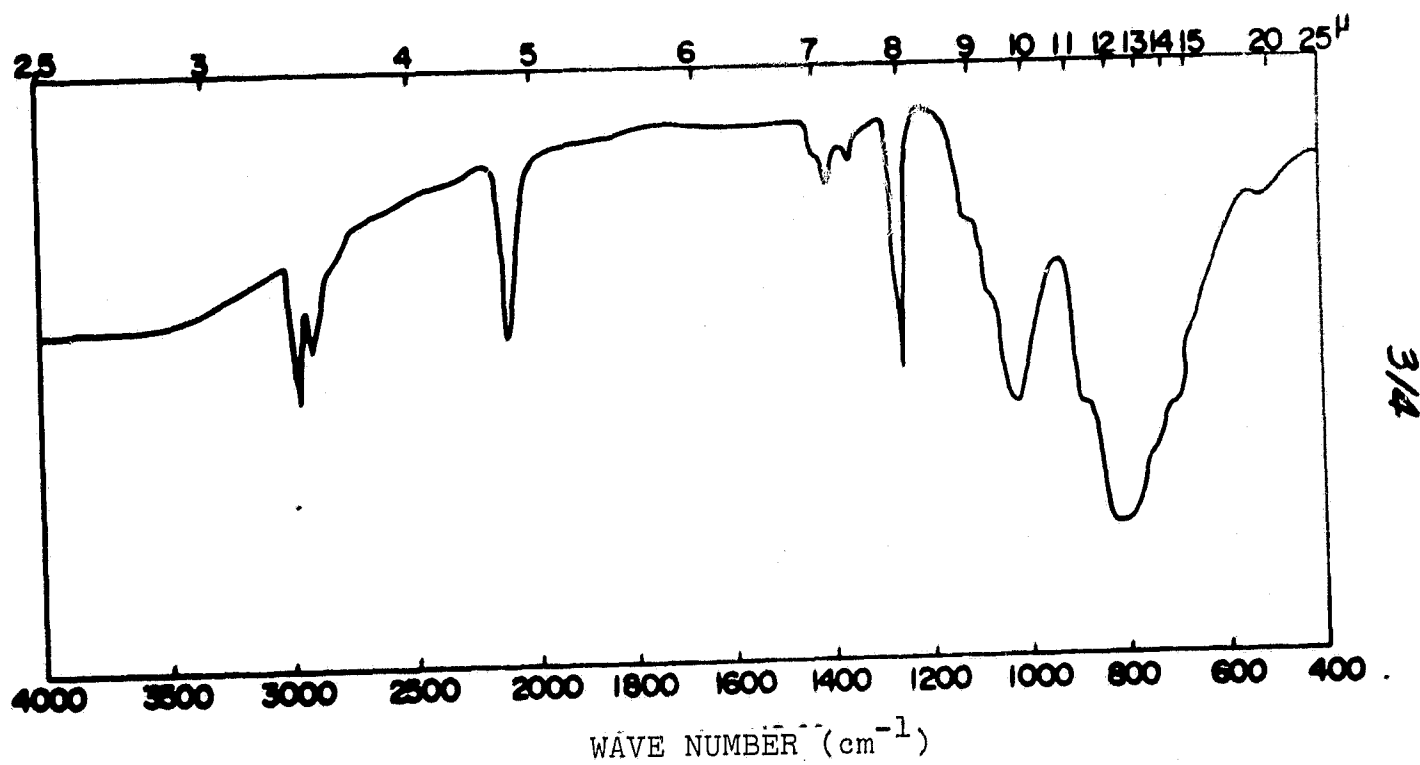


FIG. 3

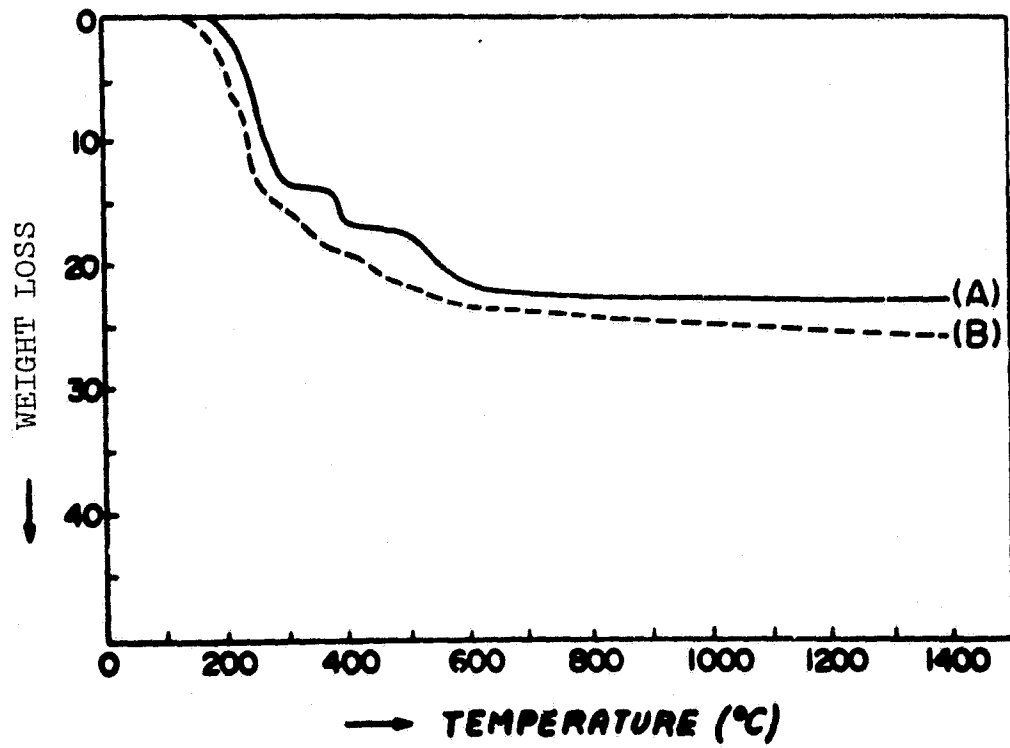


FIG. 4